

Study on rapid detection of irradiated rice based on RVA profile

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Abstract In order to confirm whether the rice sample was exposed to gamma radiation, the changes in starch pasting viscosity of rice irradiated by different absorbed doses with additive acid solution and distilled water were investigated. The peak viscosity of irradiated rice sample was significantly decreased with the increment of absorbed doses even for the samples stored over 360 days. Irradiation samples can be distinguished from non-irradiated samples by their RVA profile as in the acid solution (pH=2.5), the starch pasting viscosities of irradiated rice samples were apparently higher while the starch pasting viscosities of non-irradiated rice samples were lower than that in distilled water (pH=7.0). The irradiation absorbed dose can be estimated accurately by the regression equation constructed with peak viscosity and absorbed doses.

Key words Rice, Starch, Irradiation, RVA profile

1 Introduction

Ionizing radiations such as gamma rays, X-rays, and electron beams have been used as convenient and efficient treatment for preserving food. The minimal physical, chemical, biological and microbiological changes of irradiated foods can be detected to determine whether the food has been irradiated or not.

The international standard on 'Irradiated Food Detection Methods' proposed by EU had been approved by International Food Committee in 2004^[1-10]. These methods could be classified into chemical methods, biological methods and physical methods. The establishment of irradiation food detection method can provide standards for identifying the irradiated food from the non-irradiated samples and detecting the absorbed doses. Assessment on the irradiated food had made great achievements through extensive researches by scientists in the global. Six European standards (GC/MS, TL *et al.*) for identifying the irradiated food were adopted widely and continued to be the main methods in the long future. Four recommended standards (such as LAL/GNB, PSL *et al.*), which was approved by European Committee for

Standardization, can be used in the first round test because of simple, convenient and economic operations. Meanwhile, a simple and economical method to identify the irradiated food like ultraweak bioluminescence might attract great interest^[11].

Rice is one of the major cereals, and its main component is starch consisting of amylose and amylose. The way for rice storage is closely related to the food safety and people's health. Keeping rice fresh technique can be used to protect rice from insect infestation and microbial contamination during storage, processing, market circulation and consuming. Gamma irradiation with high penetrating power and thorough insecticide^[12] is an economical and effective way to preserve rice toward desinsection because of its high penetrating power and thorough insecticide^[12] is capable of killing the worm eggs inside the grain of rice and no smell or residual toxicity left after irradiation, it is an economical and effective way to preserve rice toward disinfection and attract increasing attentions.

There were few reports on assessing whether rice was irradiated and estimating the absorbed doses.

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In this paper, to distinguish the irradiated rice from non-irradiated rice without the reference samples, rice starches (round-shaped rice) with different absorbed doses and different solution pH value were used to investigate their pasting viscosity by Rapid viscosity analyser (RVA), which will provide some information on irradiated rice detection.

2 Materials and Methods

2.1 Sample source

Some round-shaped japonica rice were purchased from the local supermarket. The samples were divided into 5 equal portions with 50 g for each, sealed in polythene (PE) bag and stored in a drier until use.

2.2 Irradiation treatment

Rice samples were exposed to 60-Cobalt source at an ambient temperature at the Irradiation Center, Zhejiang University, Hangzhou, China. The activity of gamma radiation was 2.96×10^{15} Bq. Five doses of irradiation, i.e. 0, 1, 2, 3, 5 kGy were used with the dose rate of 0.8 kGy/h. All samples were placed with the same horizontal level with the irradiation source and irradiated in the natural temperature.

2.3 Determination of starch pasting viscosity

The samples after irradiation were ground into powders and passed through a sieve of 100 mesh size. The starch pasting viscosity was determined in duplicate by a Rapid Visco Analyser (RVA, Model-3D, Newport Scientific Inc, Australian), which was controlled by the Thermo Cycle for Windows (TCW) software (American Association of Cereal Chemists (AACC), 1998)^[13]. Rice starch 3.0 g with 14%, moisture content was weighed into the sample cup and 25 mL distilled water was added just before analysis, temperature inside the pot changed while stirring is as follows: first maintained at 50°C for 1 minute, then raised to 95°C at the rate of 12°C/min, and maintained at 95°C for 2.5 min, then cooled to 50°C, and maintained at 50°C for 1.4 min. The paddle will rotate at 960 rpm for the first 10 s, at 160 rpm till running out. The parameter values of starch pasting viscosity can be expressed by Rapid Visco Units (RVU), the following parameters such as peak viscosity (PV), hot

viscosity (HV), cool viscosity (CV), break down (PV minus HV) and set back (CB minus PV) were used as the characteristic values of RVU profile.

2.4 Detection method

Two parallel samples were selected from the starch samples without gelatinization, one was added acid solution pH=2.5, the other was added distilled water (blank experiment). All samples were stirred to uniformity at the same conditions, starch pasting viscosity of the sample was tested on the Rapid Visco Analyser, and the dynamic changes of the RVA profile were monitored. The samples were determined to be irradiated if the RVA profile was higher at pH=2.5 compared to the samples added distilled water. The samples were determined to be free from irradiation treatment if the RVA profile was lower at pH=2.5 than the samples added distilled water.

3 Results

3.1 Effect of different absorbed doses on starch pasting viscosity

The major parameters of RVA profile such as PV, HV and CV were considerably decreased with the increment of absorbed doses when the starch in rice was irradiated at different absorbed doses as listed in Table 1. It was obvious that the viscosity of non-irradiated sample was higher than that of irradiated samples. With increment of absorbed doses all of viscosity including PV, HV and CV decreased when the samples added with distilled water at pH 7. When added with the acid solution of pH 2.5, the PV was higher than that of added with the distilled water of pH 7. And there was also the PV decreased with the absorbed doses as listed in Table 2. The reductions in the values of starch pasting viscosity can be served as the reference whether the samples have been irradiated or not. Some reports suggest that starch degradation reaction resulting in the decline of the molecular weight is responsible for the decrease of starch's viscosity when the amylose and amylopectin were involved in radiation degradation of rice^[14]. Radiation can cause the cleaving of polysaccharide chains, thereby generating degradable fragments of dextrin, which is the reason for decrease of starch content^[15].

Table 1 Changes in the values of starch pasting viscosity (RVU) of rice sample after irradiation with different absorbed doses determined at pH 7

Dose / kGy	Peak viscosity (PV)	Hot viscosity (HV)	Cool viscosity (CV)
0	3015	1591	2883
1	2383	1270	2291
2	1820	820	1610
3	1396	542	1160
5	692	163	478

Table 2 Changes in the values of starch pasting viscosity (RVU) of rice sample after irradiation with different absorbed doses determined at pH 2.5

Dose / kGy	Peak viscosity (PV)	Hot viscosity (HV)	Cool viscosity (CV)
0	2797	1001	1634
1	2850	1050	1700
2	2561	757	1354
3	2353	472	960
5	1765	296	652

RVU (Rapid Visco Units): 1 RVU=12 CP

3.2 Effect of the solution pH on RVA profile

According to the method described in 2.4, the samples were equally separated into two portions, one portion was added distilled water of pH 7, another was added

the acid solution of pH 2.5. The RVA profile was determined by the Rapid Visco Analyser (RVA). As shown in Fig.1, RVA profiles at pH=2.5 were higher than those of at pH=7 for the non-irradiated rice.

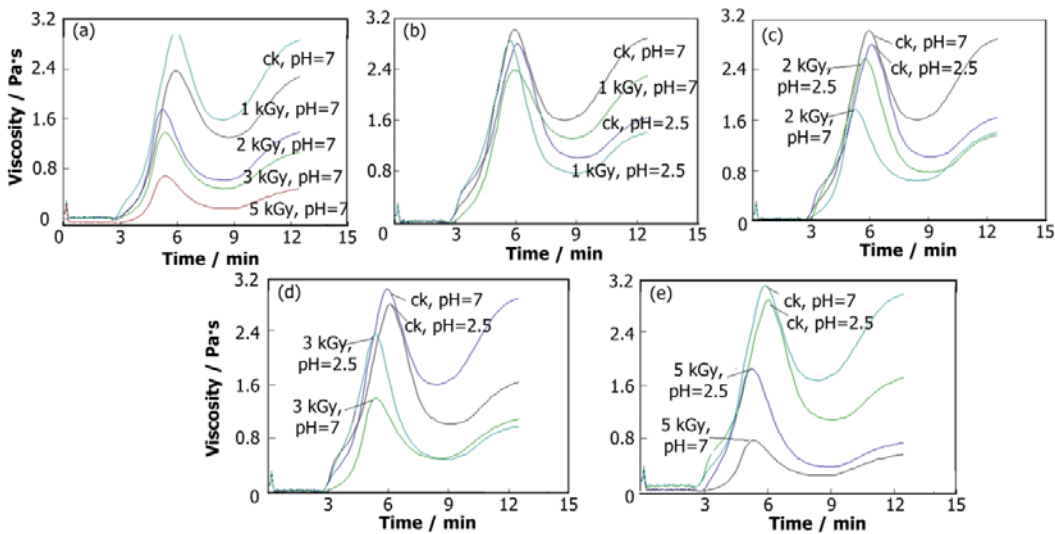


Fig.1 Effect of the solution pH on RVA profile.

However, the values of starch pasting viscosity in the irradiated samples at pH=7 were lower than those of at pH=2.5, which was still less than those of the non-irradiated counterparts. The higher of the irradiation dose, the lower starch pasting viscosity. It can be explained that hydrogen ion can cut down small polysaccharide chains caused by irradiation and

cleavage into large molecular, as a result, the molecular weight increasing compensates for the viscosity. Hence, we can easily and rapidly inspect whether starch in rice has been exposed to irradiation treatment or not with additive of acid solution to markedly alter the RVA profile.

Table 3 Changes of starch pasting viscosity (RVU) of rice samples with different absorbed doses stored for 360 days after irradiation

Dose / kGy	Peak viscosity (PV)	Hot viscosity (HV)	Cool viscosity (CV)
CK (pH 7)	2968	1768	3647
CK (pH 2.5)	2490	1084	2156
1 (pH 7)	2226	1281	2731
1 (pH 2.5)	2755	1146	2240
2 (pH 7)	1812	827	1763
2 (pH 2.5)	2445	821	1781
3 (pH 7)	1352	508	1180
3 (pH 2.5)	2220	662	1387
5 (pH 7)	618	315	775
5 (pH 2.5)	1628	463	1102

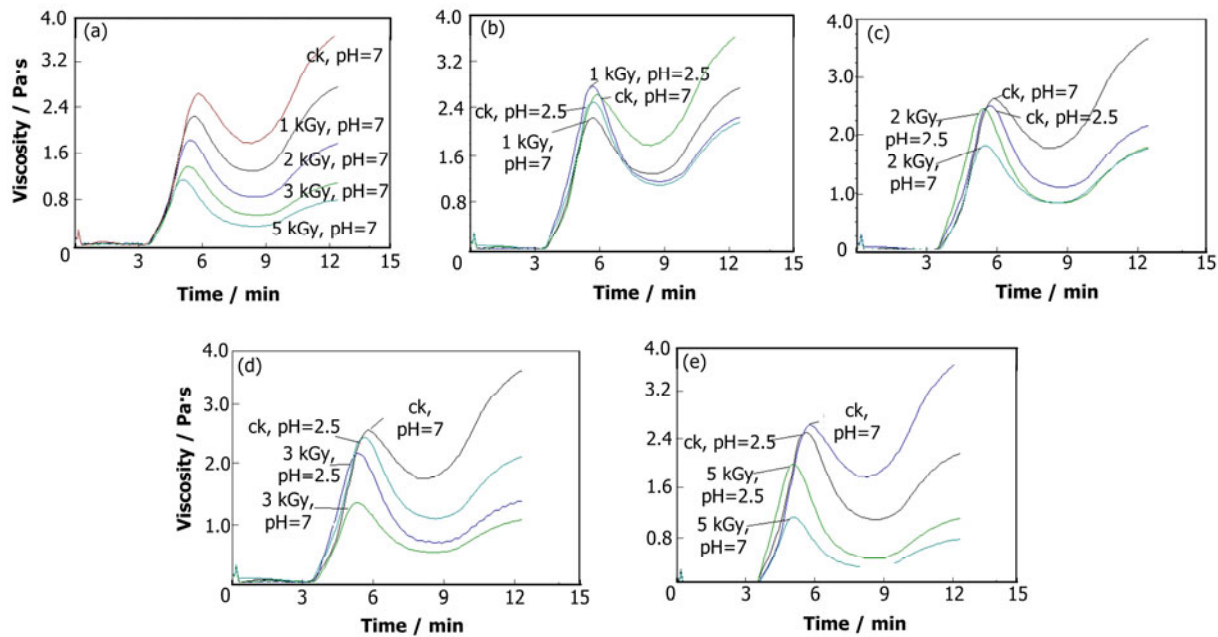


Fig.2 Effect of storage time on RVA profile.

3.3 Effect of storage time after irradiation on RVA profile

To keep breathability of rice, both the irradiated and non-irradiated samples were put into the nylon bags, respectively. The nylon bags were placed on the experiment desk and set for the stored 360 days to investigate the changes in starch pasting viscosity. It was found that, 1.56% reduction in PV value was determined after 360 days storage time in the non-irradiated sample, meanwhile there were 6.58% reduction in the sample irradiated by the dose 1 kGy, 3.25% reduction by 3 kGy, 10.69% reduction by 5 kGy as listed in Table 3. The decrease in RVA profile was also clearly observed after 360 days storage time

(Fig.2), indicating that the fragmentation of molecular chains still occurred in the irradiated macromolecules of amylose and amylopectin during the storage.

3.4 Relationship between viscosity and absorbed doses

With the regularities between PV, HV, CV and absorbed dosages, the correlation between logarithm of starch pasting viscosity (Y) and absorbed doses can be represented as follows: $Y_{pv}=3.5012-0.1277X$ $R^2=0.9920$, $Y_{hv}=3.3207-0.2139X$, $R^2=0.9916$, $Y_{cv}=3.5003-0.1575X$, $R^2=0.9868$, and the absorbed dosage can be calculated^[16]. Here Y_{pv} , Y_{hv} and Y_{cv} are the logarithm of starch pasting viscosity with PV, HV and CV respectively, and X is absorbed doses (kGy). Thus the

absorbed doses for irradiated rice samples can be calculated. When PV used, it can be suggested that it is relatively reasonable to estimate the actual absorbed doses based on the PV exponential correlation though the theoretical calculation is less than the value determined as shown in Table 4. On the other hand as shown in Table 3, the PV of irradiated rice sample with additive acid aqueous solution should be higher

than with additive distilled water meanwhile the PV of non-irradiated rice sample with additive acid aqueous solution should be lower than with additive distilled water. So in the actual practice, we could distinguish whether the samples were irradiated. If PV of rice samples was higher at the neutral conditions than those at the acid conditions, the samples were not irradiated.

Table 4 Relationship between starch pasting viscosity and irradiation dosage

Dose / kGy	Peak viscosity (PV) $Y_{pv}=3.5012-0.1277X, R^2=0.9920$			Hot viscosity (HV) $Y_{Hv}=3.3207-0.2193X, R^2=0.9916$			Cool viscosity (CV) $Y_{cv}=3.5003-0.1575X, R^2=0.9868$		
	Lg (RVU)	Dose / kGy	Relative error / %	Lg (RVU)	Dose / kGy	Relative error / %	Lg (RVU)	Dose/k Gy	Relative error/%
0	3.479	0.1738	0	3.290	0.1399	0	3.459	0.2622	0
1	3.377	0.9726	2.74	3.103	0.9927	0.73	3.360	0.8907	10.93
2	3.260	1.888	5.60	2.914	1.855	7.25	3.207	1.862	6.90
3	3.145	2.789	7.03	2.732	2.684	10.53	3.064	2.770	7.66
5	2.840	5.177	3.54	2.212	5.055	1.10	2.679	5.214	4.28

4 Discussion

4.1 Mechanism for the decrement of starch pasting viscosity caused by irradiation

Starch is mainly consists of amylose and amylopectin, amylose is commonly called chain starch. Chain starch is composed of D-anhydroglucose units linked with α -1, 4 glycosidic bond and amylopectin is composed of D-anhydroglucose units connected by α -1, 6 glycosidic bond and α -1, 4 glycosidic bond, and the branch positioned in the α -1, 6 glycosidic bond where branching taking place^[17]. The starch pasting viscosity decreased with the increment of absorbed doses (Tables 1 and 2). The irradiation with gamma rays was capable of degrading starch through the cleavage of glycosidic linkages and bonding peptide into smaller fragments, such as short aldehyde, ketone, acid chain and monosaccharide (glucose, maltose, and dextrin) *et al.*, peptide derivatives as well as amino acid and some small molecular weight fragments, then reduced in the reduced starch pasting viscosity^[18]. Water contained in the irradiated samples can generate free radicals and hydrated electron free radicals, which can react with the group in the glycosidic bond and peptide as well as the radicals generated by protein after irradiation. The starch can be further cleaved into

glycosidic bond and peptide chain through one chain reaction accelerate the decrease in starch pasting viscosity^[19]. The H· in the water can also react with the group on the aldehyde, ketone, acid, and lead to the polymerization of the short chains, which can compensate for starch pasting viscosity at certain.

4.2 Error analysis for the estimated irradiation dosage

There was relative error between theoretically calculated value and actual irradiation dose according to the regression equations (Tab. 3), the relative error between theoretically calculated value and actual irradiation dose was highest with 7.03% and lowest with 2.74% when estimated by the PV exponential correlation, highest with 10.53% and lowest with 0.73% by HV, and highest with 10.93% and lowest with 4.28% by CV. The main reasons for the error can be described as follows: at first, the error is caused by irradiation. The absorbed dose designed in the experiment is not in accordance with the actual exposed dose to sample since the samples have certain volume instead of the dose just on one dot. Second, the static irradiation processes are chosen then the sample is being treated, the inaccuracy of the actual distance between the samples and the irradiation source compared to the calculated distance can also cause

error. Third, it is necessary to correct the radioactivity of the irradiation source immediately when the samples are being irradiated. We need to make sure that the samples being irradiated should maintain on the same horizontal level with the irradiation source. Fourth, the error is caused by sampling time for detection. At last, the system error is caused by the measurement of starch pasting viscosity in the samples. Based on the analysis of the experimental data, the lower of the absorbed dose, the larger the error is, the higher of the absorbed dose is, the smaller the error is.

5 Conclusion

The change of rice starch pasting viscosity (RVA) was significant after the rice has been treated with irradiation, and the values of RVA decreased as the doses of irradiation increased. In this paper, we compared the RVA changes of the same sample tested in solutions with different pH and found out that if the samples have been irradiated, the RVA profile is higher at pH=2.5 than at pH=7.0. Otherwise the RVA profile is lower at pH=2.5. Therefore, the difference of RVA in different testing solution could be one promising method to indentify the starchy food wheather they have been irradiated or not. Also, the absorbed doses can be calculated according to the regression equation based on $PV:Y_{pv}=3.5012-0.1277X$ $R^2=0.9920$

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